ACTIVITY REPORT

August 2002

Natural Gas & Oil Technology Partnership

bringing department of energy national laboratories capabilities to the petroleum industry

Los Alamos
Los Alamos, NM 87545
(505) 667-7811

Sandia
Albuquerque, NM 87185
(505) 844-7333

Lawrence Livermore
Livermore, CA 94551
(925) 422-5196

Lawrence Berkeley
Berkeley, CA 94720
(510) 486-5085

Argonne
Argonne, IL 60439
(202) 488-2415

Brookhaven
Upton, NY 11973
(516) 344-3819

Idaho
Idaho Falls, ID 83415
(208) 526-7004

Oak Ridge
Oak Ridge, TN 37831
(865) 574-4977

Pacific Northwest
Richland, WA 99352
(509) 372-4565

To: William F. Lawson, Director
National Energy Technology Laboratory
One West Third Street
Suite 1400
Tulsa, OK 74103-3519

From: J. Albright, Los Alamos
D.J. Borns, Sandia
J. Ziagos, Lawrence Livermore
N. Goldstein, Lawrence Berkeley
D. Schmalzer, Argonne
A. Goland, Brookhaven
B. Reynolds, Idaho
T. Schmidt, Oak Ridge
B. Saffell, Pacific Northwest

cy: E. Allison, DOE Fossil Energy
L. Capitanio, DOE Fossil Energy
G. Dehoratiis, DOE Fossil Energy
A. Hartstein, DOE Fossil Energy
B. Hochheiser, DOE Fossil Energy
E. Subia-Melchert, DOE Fossil Energy
N.B. Woodward, DOE Office of Science
D. Alleman, DOE-NETL-Tulsa
J. Casteel, DOE-NETL-Tulsa
N. Comstock, DOE-NETL-Tulsa
R. Lindsey, DOE-NETL-Tulsa
R. Long, DOE-NETL-Tulsa
K. Sterling, DOE-NETL-Tulsa
D. Sutterfield, DOE-NETL-Tulsa
J. Ammer, NETL
H. Guthrie, NETL
B. Gwilliam, NETL
J. Rogers, NETL
B. Tomer, NETL
F. Toro, NETL

Note: Natural Gas and Oil Technology Partnership projects are reported according to the following schedule:

January, March, May, July, September, November	**February, April, June, August, October, December**
Drilling, Completion, and Stimulation Technology Oil and Gas Recovery Technology Diagnostic and Imaging Technology	Upstream Environmental Technology Downstream Environmental Technology Natural Gas Technology

Natural Gas and Oil Technology Partnership on the World Wide Web: http://www.sandia.gov/ngotp/

Upstream Environmental Technology

Reducing Chemical Use and Toxicity in Produced-Water Systems

(BP Amoco, Rhorback Casasco, and ANL)

No report received.

Ecological Framework to Evaluate the Effect of Size and Distribution of Releases at Upstream Petroleum Sites

(American Petroleum Institute, BP Amoco, ChevronTexaco, ExxonMobil, Gas Technology Institute, Unocal, LBNL, ORNL, and LLNL)

Highlight:

- Project researchers presented a paper and submitted two abstracts.

Project researchers continue the intensive modeling phase of the project. The goal is to develop generic models that can be used to determine the threshold frequency, size and/or distribution of brine spills that would significantly impact the persistence of herbivore and/or predator populations. Researchers also plan to use the models to quantify how the effects of exploration and production-related habitat loss differ for species with different life history attributes, mobility, and spatial habitat requirements. Models are parameterized for the Tallgrass Prairie Preserve in Osage County, OK.

Scientists at ORNL are running the individual-based badger model. After evaluating two previous algorithms for territory acquisition, a hybrid algorithm was developed that represents a good compromise between biological realism and efficiency. Researchers also modified the ORNL model to run multiple replicate simulations in stochastic mode and to report summary results. Researchers are evaluating the simulated response of badger populations to landscapes with different proportions and fragmentation of brine spills and setting up the model to perform sensitivity analysis.

LLNL scientists are also investigating alternative movement strategies for prairie voles and developing routines for sensitivity analysis. Researchers have nearly finished acquiring the necessary data to parameterize a short-eared owl model. A significant portion of the diet of the short-eared owl is the prairie vole.

Project researchers presented at paper at the July 2002 Annual Meeting of the Society for Mathematical Biology and International Conference on Mathematics and Biology, in Knoxville, TN. In addition, abstracts were submitted for the American Society for Testing Materials Symposium on Landscape Ecology and Wildlife Habitat Evaluation: Critical Information for Ecological Risk Assessment, Land-Use Management Activities, and Biodiversity Enhancement Practices, in Kansas City, MO, April 7–9, 2003 and an invited symposium on the issue of scale in ecological risk assessments at the Society for Environmental Toxicology and Chemistry annual meeting in Salt Lake City, UT, November 17–20, 2002.

Estimation and Reduction of Air Quality Modeling Uncertainties (Envair, EPRI, and LBNL)

Project researchers are concerned with evaluating and reducing uncertainties in the photochemistry in air quality models as a prototype application of exercising the modeling uncertainty framework. The researchers are investigating the temporal and spatial resolution requirements for measuring atmospheric optical properties that are necessary for the determination of key photolysis reaction rates. These rates are required for modeling ozone (smog) formation using air quality models. This is especially important since an error of 50% on the NO_2 photolysis rate results in a 20% error in ozone. The effort to determine how frequently the optical depth at a given spatial location must be updated is accomplished using time series analysis.

Researchers are working on an application to evaluate uncertainties in chemistry and emissions that result in uncertainties in modeled hydrocarbon concentrations as a function of space and time. This is important because hydrocarbon species are precursors for ozone and secondary organic aerosol formation. LBNL researchers are also directing effort to understand how model uncertainty information is used and might be successfully communicated for use in air quality planning. A number of interviews were conducted with stakeholders involved with various aspects of air quality modeling. A list of coding categories and category attributes were finalized, and the transcription and coding of the interviews was completed. LBNL researchers are also preparing a review paper describing various approaches to evaluating model uncertainty.

The LBNL team engaged in a number of technology transfer activities by presenting their research results at the NGOTP review meeting in Houston and at the annual meeting of the American Association of Aerosol Research. The Environmental Protection Agency (EPA) Associate Director of Health visited LBNL for three days in December 2001. LBNL staff briefed him on the Air Quality Model Uncertainty research to inform the EPA of the project. They also briefed staff from the California Air Resources Board and the California Energy Commission of their results.

Remote Sensing for Environmental Baselining and Monitoring (ChevronTexaco, UC-Davis, and ORNL)

Highlight:

- Field date from Jornada Experimental Range analyzed.

Project researchers are exploring the resolution limits for plant species identification. ORNL completed an analysis of 215 measurements that were made at the grass site of the Jornada Experimental Range. Each measurement is a vector consisting of 2151 values. The values represent reflectance at wavelengths ranging from 350 nm–2500 nm. Each measurement is described with one or two of the following 12 labels: "Bare", "Litter", "Aristada", "Capa", "Datu", "Forb", "Grass", "Mesquite", "Senna", "Snakeweed", "Tila", and "Yucca." Here, "Bare" represents bare soil, "Litter" represents plant litter, and the other ten labels designate plant species. Earlier, ORNL sought to determine if each of the 12 labels was associated with a distinct hyperspectral signature.

The new clustering method developed to find distinct sets of measured values, partitions the measurements into distinct groups that correspond to different stress states or species. Correlation coefficients (cij) are calculated for all of the measurement vectors. The distance (dij) between any two vectors is: cij = 1 - dij. Given a cluster radius (r), a cluster is calculated for each vector, where a cluster is a set of vectors that are neighbors of the base vector with a distance from the base vector that is less than r. The distinct groups calculated in this manner are referred to as super clusters. The first super cluster is the cluster having the largest number of neighbors. Each subsequent super cluster is the cluster that has the largest number of neighbors that are not yet included within a super cluster. The method stops adding super clusters when the maximum

number of unclustered neighbors is < 4. When r is small, the vector is the only member of the cluster and no super clusters are found. When r is large, most of the vectors are within a few super clusters. As r increases from small to large, the number of super clusters rises to a maximum, and then declines. The maximum number of super clusters is 20; this maximum occurs for a cluster radius of 0.007 (the correlation coefficients then are >0.993 for each super cluster). As the radius increases, the number of unclustered vectors that remains, after all of the super clusters were chosen, decreases monotonically. With this clustering technique and data set, the number of unclustered vectors is 55 when the number of super clusters is 20.

The super clusters are chosen to have the largest possible number of unclustered vectors, but they can also include vectors that are members of other super clusters. For the data ORNL examined, only 5 of the 20 super clusters include vectors that are members of other super clusters. The new clustering method revealed 20 (almost) distinct groups that could correspond to different stress states or species.

Modeling of Water-Soluble Organic Content of Produced Water

(ChevronTexaco, Phillips Shell, Statoil, and ORNL)

Highlight:

- Produced water characterization data successfully modeled by assuming thermodynamic equilibrium between the aqueous and hydrocarbon liquid phases.

Industry participants and ORNL embarked on a study of organic solubility in produced water, including characterization of the organic component in produced water and modeling of its solubility. The characterization of the produced water is complete, and shows that the water-soluble component is primarily polar, with a discernible trend in increased solubility with increasing pH.

Aqueous-hydrocarbon systems can be modeled in a variety of ways. ORNL used a simple liquid-liquid equilibrium model with the solubility predicted by non-random two liquid (NRTL) activity coefficients in the aqueous and hydrocarbon phases. The model was successfully used to fit the pH-dependence data generated in a crude-oil/simulated brine system. This model incorporates the acidity of the polar components, in this case assuming a composite pKa of 5.5. Results of calculations agree with the trend seen in the experimental results, where methylene-chloride extractable material (particularly C10-C20 range) become more soluble as the pH increases beyond 7. This is because of increased deprotonation in the basic aqueous phase.

The advantage of a thermodynamic equilibrium model is that changing conditions, such as temperature dependence and salinity, can be incorporated into the expressions for the activity coefficients. Volatile components and the dependence of solubility on pressure can be introduced with an additional gaseous phase, represented by an equation of state. The difficulty of formulating the model is in the selection of which components will represent the system. Uncertainties in the water characterization data preclude their use for lumped parameter properties. Questions remain as to how well binary and ternary NRTL parameters represent a multi-component system, especially one that is non-ideal. Cross-correlation, such as between salinity and pH, was also not investigated in the characterization project.

Science-Based Methods to Assess Risks Attributable to Petroleum Residues Transferred from Soil to Vegetation

(ChevronTexaco, UC-Berkeley, UC-Davis, and LBNL)

Highlights:

- New FY02 project--funding was received and research began in May 2002.
- The revised plant uptake model was completed.
- The revised model was compared to the existing empirical model and results were presented at the International Society of Exposure Analysis conference.

Risk assessments of contaminated soils rely on models that link soil residue levels to exposure concentrations in edible plant parts. These models use simple plant-soil partition coefficients or empirical relationships based on a limited number of chemicals. The models ignore transformation/sequestration processes and variations among vegetation types. As a result, linking chemical residues in soil to exposure concentrations has a level of uncertainty that is extremely high. By reducing these critical uncertainties, this project will improve the reliability of risk assessments where the critical and (often) most uncertain element is the accumulation of chemicals in plants.

Project researchers met to discuss the availability of plant uptake data, the status of the revised plant uptake model under development at LBNL, possible test chemicals, and relevant plants/soils to include in the modeling and experimental phase of the study. The preliminary list of chemicals for the modeling phase include benzene, toluene, ethylbenzene, xylenes, polycyclic aromatic hydrocarbons (PAHs) ranging in molecular weight from naphthalene to indeno(1,2,3-c,d)pyrene and a selection of high molecular weight alkanes.

LBNL researchers surveyed scientific literature and completed development of a revised mass balance model that brings together existing and newly available information related to plant uptake. The revised model was incorporated into a multimedia fate and transport modeling framework providing a fully coupled soil-plant-air system. This effort provides the basis for comparing existing tools used to support regulatory decisions, to the range of mechanistic, theoretical and empirical models that are available to describe plant uptake. Predicted soil-plant bioconcentration factors (BCFv) from the revised plant model were compared to predictions from the empirically derived Travis and Arms model (Travis and Arms, 1988) for a set of 300+ chemicals. The two models compare reasonably well for pesticides, which represent the bulk of the original Travis and Arms data set, but differ significantly for hydrocarbons and other non-pesticide chemicals. A suite of sensitivity analysis tools, including some developed by LBNL researchers, are being used to evaluate results from the model comparison.

The experimental phase of the research is also under way. A detailed set of chemical extraction methods for plants, developed in Professor. Kevin C. Jones' laboratory in Lancaster, UK, was obtained and researchers at the University of California-Davis are continuing to work on optimizing these extraction and analysis methods for PAHs and various plant tissues in preparation for commencing work with the exposure chambers.

Downstream Environmental Technology

Kinetics of Biochemical Upgrading of Petroleum

(Biocat, ChevronTexaco, Shell, and BNL)

No report received.

A Predictive Model of Indoor Concentrations of Outdoor $PM_{2.5}$ in Homes

(Aerosol Dynamics, Western States Petroleum Association, and LBNL)

Progress was made on two modeling fronts. Project researchers completed initial testing of a physics-based model to calculate rate constants for aerosol-to-gas vaporization and gas deposition on building surfaces. The modeled rate constants are being incorporated into a transient model for nitrate aerosol vaporization that will be compared with measured concentrations of ammonium nitrate aerosol and gaseous nitric acid and ammonia. Second, a transient model of indoor aerosol concentrations of outdoor origin was employed as response function in a regression model to determine the best-fit for the penetration and deposition rates for nitrate, sulfate, and total carbon constituents of indoor aerosols. Initial results for sulfate are consistent with previously published results for penetration and deposition rates. Analysis for total carbon and nitrate are continuing. This work is being extended to include analysis of black carbon and the size resolved aerosol data.

The manuscript entitled " Automated Measurements of Ammonia and Nitric Acid in Indoor and Outdoor Air" by Marc L. Fischer, David Littlejohn, and Nancy J. Brown was submitted to *Environmental Science and Technology*.

A Predictive Model of Indoor Concentrations of Outdoor Volatile Organic Compounds in Homes

(American Petroleum Institute, Western States Petroleum Association, and LBNL)

In response to the need to put the regulations for hazardous air pollutants (HAPs) on a risk basis, LBNL designed and has nearly completed coding for a coupled outdoor/indoor air model. This will provide a tool for assessing the exposure to indoor HAPs of outdoor origin. The first generation of this model had an outdoor sub-model based on a Lagrangian photochemical box model. The researchers implemented the chemical mechanism, SAPRC-99, into the model because it is the best representation of atmospheric volatile organic compound (VOC) chemistry. A set of diurnally-varying emissions representative of an urban area was used as model input for the outdoor portion. Dilution and entrainment of air aloft due to cell height variations induced by a temporally-varying mixing height are included in the model. A state-of-the-art radiation model is included in the model to calculate actinic flux that drives the photochemistry. Project researchers added the ability to treat indoor surface chemistry and modified the time-dependent species mass-balance equations to include air exchange and surface adsorption and desorption. The user interface was improved to allow the choice of indoor or outdoor run, the air exchange rate, the number of interior surfaces and their surface-to-volume ratios, and the adsorption and desorption rates for each species of interest. The base chemical mechanism, SAPRC-99, was modified to include several species of interest explicitly, namely, benzene, toluene, xylene, naphthalene, acrolein, butadiene, and MTBE. Evaluation of the code is proceeding.

Project researchers tested the apparatus to investigate sorption dynamics of individual hazardous air pollutants on individual indoor surfaces in order to supplement data from other studies. A series of experiments to screen previously untested volatile HAPs for sorptive interactions with indoor surfaces was initiated. Researchers examined the transport of acetaldehyde, acrolein, 2-butanone (methyl ethyl ketone) and benzene, along with the previously tested ethylbenzene in a furnished 50-m3 chamber.

The Environmental Protection Agency Associate Director of Health visited LBNL in December for a project briefing. The principal investigator visited the EPA at Research Triangle Park in February to learn of their research on HAPs.

Developing Enzyme and Biomimetic Catalysts for Upgrading Heavy Crudes via Biological Hydrogenation and Hydrodesulfurization

(ChevronTexaco, ORNL, and ANL)

Highlight:

- An invention disclosure was submitted on development of the Ni-Fe active center peptide as a hydrogenation biocatalyst.

In order to develop a biocatalyst for conversion of organosulfur compounds, investigations were carried out to modify the hydrogenase enzyme, which catalyzes hydrogen splitting. A partially purified enzyme (obtained from D. gigas by purification up to the third step, i.e., the diethylaminoethyl (DEAE**)**-cellulose chromatographic separation step, as reported previously) was used in the preparation of the biocatalyst. The enzyme was digested with a protease and then separated by ultrafiltration and size-exclusion chromatography to obtain the nickel-iron active center peptide (biocatalyst). The catalytic properties of the active center peptide were studied at various temperatures and in organic-aqueous solvent mixtures. Preliminary results indicate that the active center peptide has hydrogen splitting activity up to 90°C with a maxima at 80°C (using benzyl viologen as a substrate). In addition, thermostability experiments indicate that the enzyme is active and stable for about 30 minutes at 80°C. The native enzyme, on the other hand, is active for only four minutes at 60°C. The active center peptide was demonstrated to retain activity in 10% acetonitrile and ethanol.

Additional experiments were limited by the amount of the active center peptide available. Experiments are in progress to produce up to a microgram of the active center, which would allow further experiments and molecular weight determination. Investigations into the conversion of dibenzothiophene (DBT) by the active center peptide have so far yielded inconclusive results. However, the DBT experiments conducted so far, were analyzed only by high pressure liquid chromatography (HPLC). Further analysis by gas chromatography-mass spectrometry and other techniques is necessary to better understand the reactions with organosulfur compounds.

Characterization and Reaction Behavior of Sterically-Hindered Sulfur Compounds in Heavy Crudes with Nano-Sized Molybdenum Disulfide

(ChevronTexaco, BNL, and ANL)

Synthesis of nano-sized HDS catalytic materials is presently the main activity of the project. The sonolysis unit was set up and researchers attempted to synthesize Mo-based materials. Several hydrocarbons were evaluated as solvents to optimize “cavitation”, which is critical to produce nano Mo metal particles by decomposition of molybdenum hexacarbonyl. Further in situ complexation of nano Mo with elemental sulfur yielded nano MoS_2. With a known ratio of $Co_2(CO)_8/Mo(CO)_6$, the method produced nano Co/MoS_2. Sonolysis of $Mo(CO)_6$ in the presence of $y\text{-}Al_2O_3$, produced supported nano Mo, i.e., nano $MoS_2/y\text{-}Al_2O_3$. The yields of all three nano-sized materials are > 90%, based on the starting $Mo(CO)_6$. Each material was produced in several-gram quantities.

The characterization of these nano materials is a key issue. The samples are being characterized at the National Synchrotron Light Source (NSLS) at BNL and Advanced Photon Source (APS) at ANL. The measurement of these materials is a challenge. Preliminary x-ray diffraction (XRD) data show that the prepared materials indeed are nano-sized. Transmission Electron Microscopy (TEM) with a resolution of 0.16 nm is being used to measure the morphology and particle size of the samples.

After necessary modifications, a shake-down of the HDS unit at ANL was completed. Preliminary catalytic activity data of these nano materials are being collected for comparison with the commercial micron-sized MoS_2. The characterization and activity data will be the subject of the next report.

Development of a Solid Catalyst Alkylation Process Using Supercritical Fluid Regeneration

(Marathon-Ashland and INEEL)

No report received.

Biocatalytic Alkane Transformation

(ChevronTexaco and LBNL)

A menu of biocatalytic agents capable of transforming alkanes to alcohols and acids was developed in a previous Partnership project (Biological Upgrading of Heavy Oils). In this project, several of the most promising biocatalysts have been selected from the menu for further characterization and development. All of the biocatalysts selected for this project harbor enzymes that fall in the well characterized AlkB family of proteins, but the biocatalysts exhibit a diverse range of activities. The objective of this project is to determine if it is genetic or physiological properties that govern the target specificity of the biocatalyst. Experiments are being conducted to measure the transformation kinetics of alkanes in whole cells and cell extracts to differentiate genetic from physiologic controls in target specificity. The genetic code of the alkane transforming enzymes will determined and the relationship between the gene code and the enzyme specificity will be investigated.

In the last two months, Biocatalyst IP-9 was positively identified as Rhodobacter ruber by 16s RNA sequencing. This biocatalyst has been tested for the presence of multiple enzymes using a catabolic inhibition assay. Results to date indicate that the organisms harbors one enzyme system that catalyzes all alkanes, rather than multiple enzymes with narrower specific ranges. The enzymes harbored by this biocatalyst are capable of transforming a broad variety of other compounds including nitriles and chlorinated solvents. In the next quarter, priority will be given to conducting a more complete genetic characterization of this biocatalyst.

Secondary Organic Aerosol Research

(Aerosol Dynamics, Western States Petroleum Association, and LBNL)

Instruments were deployed near the University of California Blodgett Forest Research Station (elevation: 1315 m). Aerosol measurements (time resolution of 2–5 minutes) consist of total particle counts using a TSI 3022A condensation particle counter (CPC), an Andersen RTAA-900 aethalometer and an OPTEC NGN-2 nephelometer. Particle size distribution data with a time resolution of one minute is collected with a TSI 3071 differential mobility analyzer and a TSI 3760 condensation nucleus counter. The sizing system measures the concentrations of 60 size bins of particles from 10–420 nm. This enables researchers to observe the formation and growth of secondary organic aerosols (SOA) from the ultra-fine to the accumulation mode.

The aerosol data are being analyzed as they become available (typically every two weeks). The particle size distribution data show several episodes of particle formation each occurring around noon. Correlations with meteorological data show that formation events occur when temperature is lower and relative humidity is higher when compared to days when particle formation was not observed. Nighttime and morning ozone levels are also higher on days when particle formation is observed.

Natural Gas Technology

225° C MWD Using Silicon-On-Insulator (SOI) Electronics

(Baker Oil Tool, Eagle-Picher, Honeywell SSEC, General Atomics, Noble Engineering, Quartzdyne, and SNL)

New FY02 project: Reporting will start three months after the DOE FY02 funding arrives at the laboratories.

Coil-Tubing-Deployed Hard Rock Thermal Spallation Drill and Cavity Maker

(Nextant, NM Tech, and LANL)

New FY02 project: Reporting will start three months after the DOE FY02 funding arrives at the laboratories.

Molecular Engineering: Next Generation of Gas Purification Technology

(ChevronTexaco, Virginia Commonwealth U, and BNL)

New FY02 project: Reporting will start three months after the DOE FY02 funding arrives at the laboratories.

Scintillating Fiber Neutron Detectors for Well Logging

(PNNL)

New FY02 project: Reporting will start three months after the DOE FY02 funding arrives at the laboratories.